Liquid Crystal Thermosets, A new Generation of High Performance Liquid Crystal Polymers

Liquid crystal polymers can now be used as resins for textile composites

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One of the major challenges for NASA's next generation reusable launch vehicles (RLVs) is the design of a cryogenic lightweight composite fuel tank. Potential matrix resin systems need to exhibit a low coefficient of thermal expansion (CTE), good mechanical strength, and excellent barrier properties at cryogenic temperatures under load. In addition, the resin system needs to be processable by a variety of non-autoclavable techniques such as vacuum bag curing, resin transfer molding (RTM), vacuum assisted resin transfer molding (VaRTM), resin film infusion (RFI), pultrusion, and advanced TOW placement (ATP).

To meet these requirements, NASA Langley Research Center has designed a new family of wholly aromatic liquid crystalline resins with a wide range of processing capabilities. Thermotropic liquid crystal polymers (LCPs) are a well-known class of engineering plastics with excellent physical properties, high mechanical strength in the direction of orientation, outstanding barrier properties, and low viscosity during processing. Although most commercial available LCPs are synthesized from aromatic monomers, they exhibit low glass-transition temperatures (Tg) and low moduli (E') at elevated temperatures. One potential solution to this problem is the design of densely cross-linked anisotropic networks. Several low-molecular weight mesogenic structures, end-capped with different reactive functionalities displayed high Tg's and high rubbery moduli. This approach, however, has several disadvantages, such as small processing windows and poor mesophase behavior.

The Advanced Materials and Processing Branch (AMPB) at NASA Langley Research Center has developed a new family of wholly aromatic liquid crystal oligomers that can be processed and thermally cross-linked while maintaining their liquid crystal order. All the monomers were polymerized in the presence of a cross-linkable unit using an environmentally benign melt condensation technique. This method does not require hazardous solvents and the only side product is acetic acid. The final product is obtained as a powder or granulate and has an infinite shelf-life. The obtained oligomers melt into a nematic phase and do not exhibit isotropization temperatures ($T_i > T_{dec}$). Three aromatic formulations were designed and tested, and include esters, ester-amides, and ester-imides.

One of the major advantages of this invention, named LaRC-LCR or Langley Research Center-Liquid Crystal Resin, is the ability to control a variety of resin characteristics such as melting temperature, viscosity, and the cross-link density of the final part. Depending on the formulation, oligomers can be prepared with melt viscosities in the range of 10-10.000 poise (100 rad/s), which can easily be melt-processed using a variety of composite processing techniques. This ability allows NASA to provide custom-made matrix resins that meet the required processing conditions for a cryogenic fuel tank. Once the resin is in place, the temperature is raised to 375 ^{o}C and the oligomers are cross-linked into a high Tg nematic network without releasing volatiles.

LaRC-LCR can also be used in thermoforming techniques where short holding-times are desired. The resin can be partially cross-linked during production until a pre-specified viscosity has been reached and this resin can subsequently be used to spin fibers or injection mold films and complex parts. The figure shows the LaRC-LCR resin in powder form and examples of neat resin and carbon composite structures.

Several products made from LaRC-LCR include films, plaques, foams, uniaxial carbon fiber pregpreg, and carbon fiber composites.

The mechanical properties of the fully cross-linked, quasi-isotropic, neat resin plaques or films are comparable to commercially available epoxy resins. Typically the ester-based resins show better toughness (modulus = 3 GPa and 3% elongation) while ester-amide-based and ester-imide-based resins appear stiffer and less ductile (modulus ~5 GPA and 1% elongation). Initial processing studies on a 6 ply, T650 carbon fiber composite (40% resin) resulted in a modulus of 74 GPa and a flex-strength of 553 MPa. Optical microscopy and scanning electron microphotography confirm excellent fiber wet-out. Mechanical properties, however, are expected to improve when we have optimized our processing cycle.

NASA-LaRC also investigated the usefulness of LaRC-LCR as an adhesive. Titanium (Ti, 6Al-4V) lap-shear specimens were prepared under different bond pressure conditions. The ester-based resins form excellent adhesive bonds with lap shear values of 3435 psi. In contrast, the values for the ester-based resin are ~20 times higher than commercial available LCP resins, and with process development we expect these values to increase even more. The ester-amide-based and ester-imide-based resins gave much lower values due to their brittle nature that measured around 1700 psi.

Thin, fully cross-linked, films of LaRC-LCR were subjected to a Helium gas permeation test. The films (thickness ~4 mil) were tested in a manometric gas transmission cell where one side was exposed to 25 psi Helium gas at room temperature. The films proved to be highly effective barriers towards Helium. Typically, no Helium permeation could be detected for 24 hours. In contrast, a well-known reference material such as KAPTON™ (thickness ~2 mil) starts leaking almost immediately under similar test conditions.

Other useful physical properties of our LARC-LCR ester based resin are summarized in the table below.

Property	**Sample**	**Value**
Melting point before cure	powder	220-350 ^{o}C*
Melting point after cure	film	-
Glass transition before cure	powder	110 ^{o}C
Glass transition after cure	film	216 ^{o}C
Thermal stability	powder	5% wt loss at 455 $^{o}C/N_2$
	powder	5% wt loss at 441 ^{o}C/Air
Density–uncured	plaque	1.39 g/cm
Density–cured	plaque	1.24 g/cm
Density–cured	foam	0.68 g/cm
Thermal conductivity	plaque	0.34 W/mK at 20 ^{o}C

*Depends strongly on formulation and degree of cross-linking.

It has to be noted that to date all our results pertain to quasi-isotropic cross-linked nematic thermosets. In order to fabricate a polymer reinforced composite, which can be used under cryogenic conditions, a highly oriented liquid crystal matrix is required in order to minimize the coefficient of thermal expansion (CTE) and match the CTE of the reinforcement fiber as close as possible. To obtain a highly oriented resin in the fiber direction we are currently preparing carbon fiber based prepreg with highly oriented LaRC-LCR resins using pultrusion techniques. Large-scale composites will be fabricated and mechanically tested under load in a cryogenic environment. Additional space environment test are scheduled for the beginning of 2003 when several LaRC-LCR test specimens will be flown on ISS as part of the Materials International Space Station Experiment (MISSE). The samples will orbit for 3 years and will be exposed to atomic oxygen and high intensity ultraviolet.

Although LARC-LCR has been developed to meet NASA's needs towards the development of a next generation launch vehicle, other applications can be envisioned as well. The thermal and mechanical behavior of this material are ideally suited for electronic applications and may find use in flexible circuits, chip housing and flip-chip underfill. Another area where thermal stability and chemical resistance are highly desirable is the automotive industry. Distributor caps, fuel tanks, air intake manifolds, rocker covers, and ignition systems are among the potential applications. The low viscosity of this resin makes this material ideal for coating applications as well. Fine powders have been used in plasma spray applications and well-defined thin coatings were obtained.

This work was done by Theo Dingemans, Erik Weiser, Tan Hou, Brian Jensen, and Terry StClair at NASA Langley Research Center and funded under NASA's Reusable Launch Vehicle (RLV) research program. We like to thank Rick Smith, Sean Britton, Pert Razon, and Crystal Topping for their help with fabrication and sample testing.

This invention is owned by NASA, and a patent application has been filed. A exclusive license for its commercial development has been granted to TICONA Inc. (Summit, NJ). For further information, contact Diane Hope at the Technology Transfer Program Office (TCPO), NASA Langley Research Center, 3 Langley Boulevard, Mail Stop 200, Hampton, VA 23681-2199. E-mail: d.l.hope@larc.nasa.gov.